Lawrence Livermore Laboratory

Materials Problems in Production, Transport, and Storage of Hydrogen

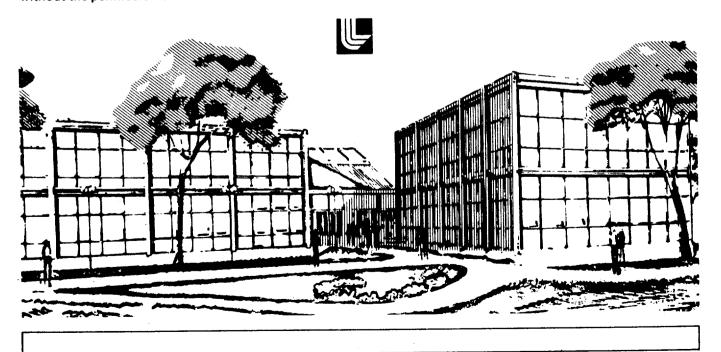
Oscar H. Krikorian

January 2, 1980

CIRCULATION COPY SUBJECT TO RECALL IN TWO WEEKS

This paper was prepared for submission to the Energy-Sources Technology Conference and Exhibition, New Orleans, LA, February 3-7, 1980

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.



DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Materials Problems in Production, Transport, and Storage of Hydrogen*

Oscar H. Krikorian Lawrence Livermore Laboratory P. O. Box 808 Livermore, CA 94550

ABSTRACT

Some of the critical materials problems that are anticipated in future hydrogen technologies are discussed here. Advanced technologies for hydrogen production include thermochemical cycles, advanced water electrolysis, and high temperature steam electrolysis. In hydrogen production by thermochemical cycles, materials problems center primarily around an $\rm H_2SO_4$ boiler, an $\rm H_2SO_4$ vapor decomposer, and an HI decomposer. Adequate materials are available for these applications, but further development is desirable to reduce fabrication and design problems and extend equipment lifetimes. In advanced electrolytic hydrogen production, the main thrust has been to raise cell efficiencies by raising operating temperatures and pressures using two approaches: (1) an alkaline electrolyte cell, and (2) a solid polymer electrolyte cell. The more extreme conditions in these advanced cells lead to the need for more corrosion resistant separator and electrode materials. Also, in order to maximize operating efficiency, new low-cost electrocatalysts are needed to reduce electrode overpotentials. It is especially desirable to reduce or even eliminate the use of noble metals as electrocatalysts to reduce costs. The future materials development of advanced electrolysis should continue to emphasize the practical problems of minimizing materials costs and extending lifetimes of reliable operation. In high temperature steam electrolysis, materials problems include development of solid state electrolytes for oxide ion conduction, and electrically conductive anode, cathode and interconnecting materials for cells.

Hydrogen transport is expected to be primarily by pipeline, and materials problems here deal with pipeline steels for transport of gaseous hydrogen. Hydrogen embrittlement is of concern, and fatigue crack growth has been identified as an important failure mode. Proper development of welding techniques is important to minimize the possibility of pipe failure at welds. Considerable work is yet needed to establish the limitations of pipeline steels for hydrogen transport.

Long term storage of hydrogen on a large scale is anticipated to be in underground repositories much as natural gas is stored today. However for short-term or small scale uses, hydrogen storage in hydrides, or storage in glass

^{*}This study was sponsored by the U. S. Department of Energy - Division of Energy Storage Systems and performed by the Lawrence Livermore Laboratory under contract No. W-7405-Eng-48.

microbaloons offer certain operational advantages, such as utility in vehicular transporation and safety. Some of the materials studies on hydride and microballoon storage are briefly mentioned in this report.

INTRODUCTION

The purpose of this report is to give a brief overview of some of the critical materials problems that we face in the development of future technologies for hydrogen production, transport, and storage. The hydrogen production technologies that will be considered here are:

- Thermochemical Cycles
- Advanced Water Electrolysis
- High Temperature Steam Electrolysis

These technologies are all based upon water as the source material for the hydogen, and non-fossil energy resources, i.e., nuclear or solar. Hydrogen produced by the above technologies is essentially a renewable resource since it reverts back to water upon its use. Hydrogen transport will be concerned with pipeline failure problems; and finally hydrogen storage will refer to the problems of storing hydrogen in metal hydride beds and in glass microspherical shells.

HYDROGEN PRODUCTION

I. Thermochemical Cycles:

Currently, there are some thirty thermochemical cycles worldwide that are under various stages of investigation and development. Energy sources that are being considered for these cycles fall into three categories: (1) high temperature gas cooled reactors (HTGR) providing a maximum temperature of $\sim\!1200\,\mathrm{K}$, (2) solar central receivers providing a maximum temperature somewhere in the 1200-2000K range, and (3) magnetic fusion reactors anticipated to provide a maximum temperature in the 1200-2000K range. Selection of an actual maximum operating temperature depends upon the process needs of the thermochemical cycle as well as an overall system design. Cycle efficiency, system economics, and materials needs are all important considerations. Electrical energy for process equipment is required in addition to high temperature process heat for operation of thermochemical hydrogen plants. For purposes of the discussion here, we will separate the materials problems related to the energy source from those related to the thermochemical plant, and the latter is all that we will discuss here.

Further, of the cycles under study, only three cycles have thus far been developed to the stage where closed loop table-top models have been built and tested in the laboratory, and those are the cycles that will be discussed here. They are illustrated in terms of their principal chemical steps and reaction temperatures in Figure 1. The main effort on the development of the Sulfur-Iodine Cycle is underway at the General Atomic Company, (1-3) for the Sulfur-Gycle at the Westinghouse Electric Corporation, (4-6) and for the Sulfur-Bromine Cycle at the Commission of European Communities Joint Research Centre-Ispra Establishment. (7-9)

a. H₂SO₄ Boiler:

One of the most critical materials problems and one that is common to all of the cycles above, is the problem of corrosion in the heat exchanger that is used to boil a concentrated azeotropic solution of H_2SO_4 . This boiling step is carried out on the $H_2O-H_2SO_4$ azeotrope that occurs at 97 wt% H_2SO_4 for the 1 MPa (10 atm) boiling point at 673K with a heat requirement for boiling of 26 kcal/mol. A high gas pressure is required from a design standpoint to minimize equipment size and gas pumping power requirements. Under these boiling conditions liquid phase H_2SO_4 is highly corrosive to all known metallic heat exhanger materials (except Pt and Au). Related to the H_2SO_4 boiling problem is the problem of concentrating the aqueous H_2SO_4 solutions that are produced in the various cycles in order to attain the 97 wt% H_2SO_4 azeotrope. The cycles as currently envisioned produce H_2SO_4 in the 50-70 wt% range. Concentrating these solutions up to 75 wt% H_2SO_4 can be accomplished by known materials and heat exchanger technology. From 75 to 97 wt% H_2SO_4 , the corrosiveness of the solutions approaches that of the boiling azeotrope, and the materials problems become essentially identical.

Materials tests in hot concentrated H_2SO_4 at 633-693K have been carried out at the Lawrence Livermore Laboratory (10,11) and at Westinghouse (6) over the past two years to identify materials that are suitable for heat exchangers and containers for the H_2SO_4 boiler. The top candidate materials from standpoints of corrosion resistance and design are the following*:

- "CrSi2" coated Incoloy 800
- SiC
- Durichlor 51 (Fe-14% Si-4% Cr)
- Silica brick

All of these materials depend upon a high silica composition, either as a surface scale or as the body of the material, for protection against corrosion.

Specimens of Incoloy 800 coated with chromium silicide of nominal composition CrSi, were tested for corrosion for 240 h at 673K in 97 wt% $\rm H_2SO_4$ at the Lawrence Eivermore Laboratory, (11) and found to show a very low rate of corrosion (extrapolates to a weight loss rate of 15 mg/cm²-y). The coatings were about 120 $_{\mu m}$ thick, uniform in thickness, well-bonded to the substrate, and without evidence of fractures. The coatings were prepared by Dr. Charles M. Packer of Lockheed Missiles and Space Company of Palo Alto, California, using a slurry coat and rapid melt technique. Although the above results are preliminary in nature, they are encouraging in that a conventional heat exchanger material such as Incoloy 800 can be protected against corrosion by a coating process.

SiC currently presents the best prospect as a heat exchanger material. Siliconized SiC (a two phase composition consisting of a mixture of SiC and Si)

^{*}Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Department of Energy to the exclusion of others that may be suitable.

is produced at the Norton $^{(12)}$ and Carborundum $^{(13)}$ companies and is especially suited for this type of application. This type of material, which contains about a 10-15 wt% excess of silicon metal, is impervious to gases, has a high thermal conductivity, high strength, good thermal shock resistance, and can be fabricated in complex shapes and bonded together to form heat exchanger assemblies. $^{(12)}$ Corrosion testing of SiC for 1121 h and Si for 592 h in 97 wt% $\rm H_2SO_4$ at 673K, at the Lawrence Livermore Laboratory showed no evidence of corrosion, $^{(10)}$ thus confirming the corrosion resistance of both SiC and Si for this application.

Durichlor 51 is a commercial high silicon cast iron material that is yet another candidate as a heat exchanger or container material. It is basically an intermetallic compound with a composition of approximately Fe₃Si, and as such presents the disadvantages common to most intermetallics of poor ductility, low tensile strength, and poor machining and fabrication characteristics. Also, being a cast material, the control of internal porosities and non-uniformities present production problems. Nonetheless, with proper quality control, and with good engineering design and practices, these problems can be controlled. From a corrosion standpoint, tests of up to 524 h on Durichlor 51 (10) have shown only a moderate amount of attack ($\sim 5~\mu m$ surface penetration), but very importantly, corrosion appears to proceed very uniformally over the surface of this material. It therefore seems reasonable to extrapolate to a lifetime of the order of 5 y for this application. In contrast to Durichlor 51, another high silicon cast iron, Duriron, shows a rather irregular corrosion behavior with grain pullouts, corrosion pits and spallation in similar H₂SO₄ corrosion tests at 673K. (10)

Silica brick is yet another acceptable material for handling of concentrated $\rm H_2SO_4$ at temperatures in the vicinity of 673K, where heat transfer is not a requirement. It would be particularly useful as a chamber liner material. The excellent thermal shock resistance of pure silica glass is well known, and it has been successfully used to contain test specimens for $\rm H_2SO_4$ corrosion tests at the Lawrence Livermore Laboratory without any evidence of corrosive attack. (10,11)

b. H₂SO₄ Vapor Decomposer:

Subsequent to boiling the H_2SO_4 azeotrope, the H_2SO_4 vapors, consisting principally of a mixture of $H_2O(g)$ and $SO_3(g)$, are passed through a vapor decomposer at 1000-1144K to give the endothermic reaction:

$$SO_3(g) \longrightarrow SO_2(g) + 1/2 O_2(g)$$
.

This vapor decomposition step is again common to the three cycles in Figure 1. In the studies thus far, a miximum process temperature of 1144K has been assumed in order to be consistant with current HTGR designs. To couple the heat output from the HTGR more efficiently with the $SO_3(g)$ decomposition, the reaction is carried out over as wide a temperature range as possible. At 1144K, $SO_3(g)$ in the presence of $H_2O(g)$ gives an $\sim\!\!80\%$ yield of $SO_2(g)$ under the anticipated operating conditions. Recycle of undecomposed $SO_3(g)$ is required to close the cycle. Ordinarily, the decomposition rate of $SO_3(g)$ is unacceptably slow below $\sim\!\!1123$ K, so that catalysts are required to achieve the necessary reaction velocities at the lower temperatures. The materials problem for the H_2SO_4 vapor decomposer therefore has two aspects: (1) selection of corrosion resistant metal alloys for a heat exchanger to transfer heat from the high temperature helium gas output of an HTGR to the H_2O/SO_3 vapor stream, and (2) selection of catalysts for decomposition of $SO_3(g)$ in the 1000-1123K range.

Corrosion tests on a number of heat exchanger alloys for the $\rm H_2SO_4$ vapor decomposer have been carried out at Ispra(9) and at the General Atomic Company(3) at temperatures in the 773-1173K range. Their latest results(14) indicate that as bare uncoated alloys, Incoloy 800H and Inconel 625 provide the best materials with anticipated lifetimes of a few years.

A substantial gain in lifetime can be achieved by using an aluminide-coated Incoloy 800H. This gives an unusually stable coating-substrate combination that stablizes in coating thickness and weight change after an exposure of 200-300 hours to the gaseous $\rm H_2SO_4$ products. (3,14) Corrosion protection is apparently afforded by an $\rm Al_2O_3$ film, and imperfections in the coating are self-healing. The useful life of aluminide-coated Incoloy 800H for this application is believed to be of the order of 20 years.

High silica materials, such as those considered for the $\rm H_2SO_4$ boiler, are also believed to be compatible with the gaseous $\rm H_2SO_4$ products. In general, concentrated liquid $\rm H_2SO_4$ is considerably more corrosive to containment materials than gaseous $\rm H_2SO_4$, even when the gases are at substantially higher temperatures.

c. HI Decomposer:

The Sulfur-Iodine Cycle (see Figure 1) involves an endothermic step in which HI (as liquid or gas) in the presence of excess iodine (60-82 wt%) needs to be heated from room temperature to $\sim\!573\mathrm{K}$ where it undergoes partial decomposition to form either liquid or gaseous iodine and hydrogen. The decomposition yield per pass is somewhere in the 10-45% range depending on process conditions, so that recycle is required for complete conversion. Some water is initially present in the HI_v, and needs to be removed during processing.

A wide range of metals, alloys, plastics and elastomers have been tested in the presence of ${\rm HI}_{\rm X}$ at room temperature, and a number of metals and alloys at higher temperatures.(3) A reasonable selection of corrosion resistant materials in all categories have been found at room temperature, and will not be detailed here. At the higher temperatures, most nickel and iron base alloys and some non-metallic materials corrode rapidly, while refractory metals and their alloys generally show good corrosion resistance. The best metallic materials are Ta, Mo, Nb-1% Zr, and a variety of Zr alloys. Zr alloys offer the best prospects from a cost standpoint. Ceramics and glasses are generally excellent. If water is removed from the ${\rm HI}_{\rm Y}$, Hastalloy B-2 also becomes a compatible alloy.

d. General Comments on Thermochemical Cycles:

I have given a description above of some of the critical materials problems today for the most advanced thermochemical cycles. Clearly this is a rapidly changing field, and as cycles evolve, the problems change. For example, I've chosen to emphasize the corrosive nature of liquid and gaseous $\rm H_2SO_4$. Some workers are currently suggesting that oxides such as $\rm Bi_2O_3$ or $\rm ZnO$ be added to $\rm H_2SO_4$ to form a solid sulfate, which would be dried and thermally decomposed to regenerate metal oxide and form the desired $\rm SO_2$ and $\rm O_2$ products. (15,16) This bypasses the materials problem for $\rm H_2SO_4$ altogether, but introduces new problems in the handling of the solid sulfates. The reader should also recognize that a large number of new cycles continue to be under investigation, and one or more of these may subsequently prove to be superior to those considered here. In general, I believe that materials problems introduced by thermochemical cycles

may differ from time to time in degree, but not in kind from those encountered in other industrial processes, such as for example, coal gasification.

II. Advanced Water Electrolysis:

The current state of water electrolysis technology, and the materials problems encountered in the development of advanced electrolysis processes have been summarized recently in a number of reports. (17-19) Most of the detailed information here draws upon reference 18. There has been little change in conventional electrolysers for the past 70 years. Electrolysers are generally built in 1-2 MW modules and operate at atmospheric pressure at a temperature of $\sim\!353\text{K}$. Usually they incorporate a bipolar design using Fe cathodes, Ni or Niplated Fe anodes, an aqueous 20-30 wt% KOH electrolyte, and an asbestos diaphragm to separate the cell compartments. These cells require $\sim\!2$ V to operate at a current density of 2000 A/m² at 353K.

Two approaches have been taken in the development of advanced electrolysis. One approach is to extend the conventional alkaline electrolyses cell to higher temperatures and to produce product gases at higher pressures, thus improving cell efficiency by reducing both the standard cell voltage and the overvoltages at the electrodes and providing more gas output per unit electrode area. The other approach is to use a solid polymer electrolyte (SPE) with the requirement that only feed water needs to be circulated. The SPE cell would also be operated at high temperatures and pressures to attain a more efficient operation. In both approaches, the goals are to increase operating temperatures to about 423K and pressures to about 3-5 MPa. As temperatures and pressures are raised, new materials are needed to meet the more severe operating conditions, and the trade-offs between material costs and operating efficiencies become very important.

a. Alkaline Electrolysers:

As the temperature is raised above about 373K in the alkaline electrolyser, the asbestor gas separator diaphragm becomes severely attacked by the alkaline electrolyte, and finding a substitute material for asbestos becomes one of the most significant materials problems for this approach. More than 50 membrane materials, including ion exchange membranes, porous material membranes, woven materials, polypropylene felts, etc., have been evaluated, and the most promising materials have been found to be Nafion and Teflon-bonded potassium titanate paper. Nafion is a perfuorocarbon sulfonate cation exchange membrane, produced by the E. I. duPont deNemours Company, that has shown the better performance characteristics, but its high cost (about \$325/m²) is a matter of concern. It may be advantageous to use NaOH as the electrolyte if Nafion is used, because ohmic losses are less across Nafion in NaOH solution than in KOH solution.

Another very significant area of materials research for alkaline electrolysers is development of electrode materials and electrocatalysts to lower the overpotentials at the electrodes and increase cell efficiency. For the cathode, two electrode materials that have recently shown promise relative to the conventional nickel cathode, are a nickel boride (developed by Deutsche Automobile Gesellschaft Forschungs Laboratorium in Esslingen, Germany), and sintered nickel electrodes impregnated with cobalt molybdate. At the anode, recent emphasis has been on developing oxide catalysts with high surface areas. Semiconducting oxides of the spinel or perovskite structures such as ${\rm NiCo_2O_4}$ and ${\rm Ba_2MnReO_6}$ are of particular interest. Teflon bonded ${\rm NiCo_2O_4}$ electrodes

have shown good performance, but the stability of the Teflon bonding is poor, and further development is needed. Other anode materials that have shown promise are sintered nickel impregnated with nickel hydroxide, and a 50 wt% Ni-50 wt% Fe alloy that has been found to show good corrosion resistance in the strong alkaline environment.

b. SPE Electrolyser:

Current SPE electrolyser designs utilize Nafion (about 0.3 mm thick) as the solid electrolyte. Charge transfer through the membrane occurs by transport of hydrated hydrogen ions $(H^{+} \cdot xH_{2}0)$ which move through the solid electrolyte by passing from one fixed sulphonic acid group to the adjacent one. Teflon bonded Pt black in the form of fine particles is pressed into one face of the Nafion membrane to form the cathode, and a noble metal alloy is similarly pressed into the other face to form the anode. An electrically conductive material is further attached to each face of the Nafion membrane and provides for several functions: (1) it functions as a separator material and permits the alternate stacking of SPE cells so that the cathodes and anodes alternate, (2) it functions as the electrical current carrier in a bipolar cell configuration, (3) it provides the channels for circulation of deionized water through the electrolyser and for removal of the H2 and 02 products. The SPE electrolysers offer advantages of a very high current density, $10,000-20,000 \text{ A/m}^2$ at 1.5-1.6 V when operating at 423K. The disadvantages center around the current high costs for Nafion and for noble metal catalysts. Bench-scale studies, with lowering of costs a major goal, are currently underway on an SPE electrolyser system at the General Electric Company. (20)

Materials investigations for SPE electrolysers include (1) a continuing search for low cost SPE materials, (2) new noble metal electrocatalyst formulations that reduce the amount of high cost noble metals required, and (3) low-cost corrosion resistant collector/separator materials. The search for SPE materials is concentrated on various fluorinated organic polymer membranes, including trifluorostyrene and perfluorocarbolic acid as examples. It is not clear that suitable low cost SPE substitutes for Nafion have yet been established. The most reliable cathode catalyst appears to be Pt, and the main goal here is to prepare a catalyst formulation that reduces the amount of Pt required from about 4 mg/cm² to about 0.02 mg/cm² with minimal loss in cell performance. Catalysis at the anode can be achieved with Pt, Ir, or Ru based materials, and oxides of Ir or Ru combined with transition elements such as Ti, Ta, Nb, Zr, and W seem to provide low-cost alternatives to the use of all noble metals. The collector/separator materials are subjected to highly corrosive conditions due to (1) the acidic nature of the hydrated SPE, and (2) hydrogen embrittlement at the cathode collector. At present, molded carbon collector/ separator materials appear to offer the best potential, with low cost being an important consideration. Alloys of Zr, Nb, Ti, and Ta offer other alternatives.

HIGH TEMPERATURE STEAM ELECTROLYSIS

Hydrogen production by electrolysis of steam inherently presents the advantage of a lower electrical power requirement as compared to water electrolysis. Part of the energy is introduced thermally as the latent heat of vaporization of water, the reversible cell voltage is reduced by about 25% at 1273K, and activation overpotentials become negligibly small. The overall gain in energy efficiency may be as much as 40% over advanced water electrolysis. However, there are a number of difficult materials problems that need to be solved to make this technology competitive.(19,21,22) Designing a heat exchanger to couple with a nuclear or solar heat source and to deliver 1273K or hotter steam is in itself a critical and

difficult task. Conceptual cell designs call for special materials for a solid state electrolyte, an anode, a cathode, and an interconnecting material to permit the joining of cells in series.

A typical cell may consist of a thin-walled tube of Y_20_3 stabilized $Zr0_2$ coated on the inside with a cathode material and on the outside with an anode material. As steam is passed through the tube it undergoes the following reaction at the cathode,

$$H_20 + 2e^- \longrightarrow 0^{2-} + H_2$$

and the 0^{2-} ions are transported across the electrolyte to the anode to complete the cell reaction, i.e.,

$$0^{2-} \longrightarrow 2e^{-} + 1/2 0_2$$
.

Although Y_2O_3 stablilized ZrO_2 has been successfully used to electrolyse steam, very thin wall thicknesses are required with this electrolyte, and development of better oxide ion conductors is desirable. The cathode material is exposed to relatively reducing conditions ($p_{02} < 10^{-7}$ Pa) so that porous Ni or Co based cermets can be used. For the anode, conditions are oxidizing. To avoid the use of expensive noble metals, we must use conductive oxides that are suitably matched for thermal expansion and chemical compatibility to the electrolyte. Mixed oxides with the perovskite structure, doped to attain a high electronic conductivity, show promise as anode materials. Perovskites also show promise for the interconnecting material used to join the individual cells in series, by joining the cathode of one cell to the anode of another. Here the requirement is more severe in that the interconnecting material must retain its electronic conductive properties over the full range of oxidizing and reducing conditions.

HYDROGEN TRANSPORT

The pipeline transport of hydrogen can be considered either on the basis of pure hydrogen, or as a blend of hydrogen with natural gas. In either case, the first large-scale pipeline transport of hydrogen will likely involve existing pipelines. The initial materials studies for hydrogen transport therefore need to focus on the limitations of conventional pipeline materials, especially on materials in use as natural gas pipelines.

Studies currently underway are concerned with pipeline welding techniques $^{(23)}$ and mechanical property tests on pipeline materials under simulated operating conditions in a hydrogen environment. $^{(24-27)}$ Pipeline and mild steel alloys under study are A516-70, A106-B, AISI-304L, AISI-1015, and AISI-4340. Hydrogen embrittlement effects on strength characteristics are especially of concern. Slow crack growth has not been found to be a serious problem in materials tested to date, but fatigue crack growth does present problems. For example, two A106-B steel pipes that had been intentionally flawed and pressurized with hydrogen at 6.9 MPa for six months showed no evidence of failure, but upon repressurizing burst at $\sim\!\!3.4$ MPa. $^{(24)}$ Post mortem analysis showed fatigue striations corresponding to four cycles of pressurization that the pipes had experienced. Apparently, fracture occured when the fatigue crack attained a critical length.

Welding studies using tungsten arc. electron beam, and laser beam welding techniques have shown that sound welds can be achieved by these techniques, but that welding standards significantly more rigid than current pipeline standards may be required to avoid weld defects.

A fair amount of work is yet needed to establish quantitative limits for hydrogen use in pipelines, and to provide guidance for the selection of future pipeline materials.

HYDROGEN STORAGE

Hydrogen storage is a critical link in the development of future large-scale utilization of hydrogen. Storage is necessary for smoothing out the mismatches of supply and demand. It is most important at the distribution sites, especially if it is used as a fuel. For storage on a large scale, probably the best choice is underground storage, and potentially, underground natural gas storage sites can be converted to hydrogen storage as natural gas resources decline.

To supplement underground storage of hydrogen, various options and their approximate installed capital costs are as follows:(24)

Storage Option	Capital Cost (\$/GJ)
Gas Storage Tanks (above ground)	1000
Cryogenic Storage (large-scale)	75
Cryogenic Storage (small-scale)	1400
Hydride Storage	3400
Glass Microballoon Storage	30

Although operating costs should also be considered, the general conclusion does not change, i.e., for large storage systems cryogenic and glass microballoon storage seem to have a definite economic advantage. The comparison is not entirely certain however, since work on glass microballoon systems is in its infancy and cannot yet be evaluated. From a safety standpoint, glass microballoons should have a distinct advantage over cryogenic systems. Hydride storage is the most costly option, but for vehicular transportation, especially with safety in mind, it remains important. Thus, materials work on hydrogen storage for future applications is currently oriented mainly toward hydride systems development, with some exploratory work being initiated on glass microballoon systems. The hydride system that has undergone the most development is based upon TiFe_{0.9}Mn_{0.1}H_x.(28) Glass microballoon studies have been carried out on microballons of about 25 μm in diameter, $\sim 2 \mu m$ in wall thickness, and with a composition of 80.9% SiO₂, 2.3% B₂O₃, 8.6% CaO, and 8.2% Na₂O, all in mole %.(29) These microballoons are filled by pressurizing them externally with hydrogen at 20-40 MPa and 500-700K, under which conditions the hydrogen diffuses through the glass walls and fills the microballoons. Upon cooling to room temperature, the hydrogen is entrapped in the microballoons under pressure, and can then be released as needed by reheating to $\sim 500 K$.

REFERENCES:

- 1. J. H. Norman, K. J. Mysels, D. R. O'Keefe, S. A. Stowell and D. G. Williamson, "Chemical Studies on the General Atomic Sulfur-Iodine Thermochemical Water-Splitting Cycle," in <u>Hydrogen Energy System</u>, <u>Proceedings of the 2nd World Hydrogen Energy Conference</u>, <u>Zurich</u>, <u>Switzerland</u>, <u>21-24 August 1978</u>, Vols. 1-5, edited by T. N. Veziroglu and W. Seifritz, Pergamon Press, Oxford, 1979, p. 513.
- 2. J. D. de Graaf, K. H. McCorkle, J. H. Norman, R. Sharp, G. B. Webb, and T. Ohno, "Engineering and Bench-Scale Studies on the General Atomic Sulfur-Iodine Thermochemical Water-Splitting Cycle," ibid., p. 545.

- 3. P. W. Trester and S. S. Liang, "Material Corrosion Investigations for the General Atomic Sulfur-Iodine Thermochemical Water-Splitting Cycle," ibid., p. 2113.
- 4. G. H. Farbman, "The Westinghouse Sulfur Cycle Hydrogen Production Process: Program Status," ibid., p. 2485.
- 5. R. L. Ammon, G. H. Farbman, G. R. Folser, C. C. Hardman, J. F. Pierre, and G. O. Yatsko, "The Westinghouse Sulfur Cycle Hydrogen Production Process: Technology Development, Status," unpublished paper presented at the Second World Hydrogen Energy Conference, Zurich, Switzerland, 21-24 August 1978.
- 6. R. L. Ammon, G. Yatsko, A. Irwin, and G. H. Farbman, "Materials Consideration for the Westinghouse Sulfur Cycle Hydrogen Production Process," ibid.
- 7. D. van Velzen, H. Langenkamp, G. Schuetz, D. Lalonde, J. Flamm, and P. Fiebelmann, "Development, Design and Operation of a Continuous Laboratory-Scale Plant for Hydrogen Production by the Mark-13 Cycle," loc. cit., reference 1, p.649.
- 8. G. H. Schnetz, P. J. Fiebelmann, and D. R. Lalonde, "Electrolysis of Hydrobromic Acid," ibid, p. 709.
- 9. F. Coen-Porisini, "Corrosion Tests on Possible Containment Materials for $\rm H_2SO_4$ Decomposition," ibid., p. 2091.
- 10. O. H. Krikorian, "Materials Corrosion Studies for a Sulfuric Acid Vaporizer," Lawrence Livermore Laboratory Report UCRL-81856 (Preprint), October 27, 1978.
- 11. O. H. Krikorian, "Corrosion Testing of Materials in Hot Concentrated Sulfuric Acid," Lawrence Livermore Laboratory Report UCRL-83411 (Preprint), September 27, 1979.
- 12. M. L. Torti, J. W. Lucek, and G. Q. Weaver, "Densified Silicon Carbide An Interesting Material for Diesel Applications," Technical Paper Series 780071, Society of Automotive Engineers Congress and Exposition, Cobo Hall, Detroit. February 27-March 3, 1978. See also brochures of the Norton Company, Worcester, Massachusetts on "Noralide Advanced Ceramics," and "Ceramics for Energy."
- 13. Edwin Craft, Carborundum Company, Niagara Falls, New York, private communcation regarding bending of KT-silicon carbide to form U-tubes, October, 1979.
- 14. P. W. Trester (General Atomic Company) and F. Coen-Porisini (Joint Research Centre Ispra), private communication, September, 1979.
- 15. M. G. Bowman, K. E. Cox, J. D. Farr, W. M. Jones, and C. L. Peterson, "Thermochemical Processes for Hydrogen Production, October 1, 1978-March 31, 1979," Los Alamos Scientific Laboratory Report LA-7937 (Progress Report), September 1979.
- 16. P. K. Hosmer and O. H. Krikorian, "Solar Furnace Decomposition Studies of ZnSO₄," Lawrence Livermore Laboratory Report UCRL-83634 (Preprint), November 20, 1979.
- 17. A. Menth and S. Stucki, "Present State and Outlook of the Electrolytic $\rm H_2$ -Production Route," loc. cit., reference 1, p. 55.

- 18. P. W. T. Lu and S. Srinivasan, "Advances in Water Electrolysis Technology with Emphasis on Use of the Solid Polymer Electrolyte," J. Appl. Electrochem. 9, 269 (1979).
- 19. G. Imarisio, "The R and D Programme of the European Communities in the Field of Hydrogen: Progress and Results," Int. J. Hydrogen Energy 4, 371 (1979).
- 20. L. J. Nuttall and J. H. Russell, "Solid Polymer Electrolyte Water Electrolysis Development Status," loc. cit., reference 1, p. 391.
- 21. W. Doenitz, R. Schmidberger, E. Steinheil, and R. Streicher, "Hydrogen Production by High Temperature Electrolysis of Water Vapour," ibid., p. 403.
- 22. J. A. Fillo, J. R. Powell, M. Steinberg, F. Salzano, R. Benenati, V. Dang, S. Fogelson, H. Isaacs, H. Kouts, M. Kushner, O. Lazareth, S. Majeski, H. Makowitz, and T. W. Sheehan, "Hydrogen Production from Fusion Reactors Coupled with High Temperature Electrolysis," ibid., p. 1135.
- 23. J. Mucci and J. A. Harris, Pratt and Whitney Aircraft Group, Government Products Division, West Palm Beach, FA 33402, "Evaluation of Laser Welding Techniques for Hydrogen Transmission," paper presented at the U. S. Department of Energy Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Sheraton International Conference Center, Reston, VA, November 13 and 14, 1979.
- 24. W. R. Hoover, J. J. Iannucci, J. R. Spingarn, S. L. Robinson, and R. E. Stoltz, Sandia Laboratories, Livermore, CA 94550, "The Hydrogen Caompatibility of Structural Materials for Energy Storage and Transmission," ibid.
- 25. H. F. Wachob, Failure Analysis Associates at NASA-Ames Research Center, Materials Science and Application Office, Moffett Field, CA 94035, "The Influence of Ferrous Microstructure on the Fatigue Crack Growth Rate in Air and in Hydrogen," ibid.
- 26. M. R. Louthan, Jr., R. P. McNitt, T. A. Adler, J. Murali, and P. E. Smith, Virginia Polytechnic Institute and State Unversity, Blacksburg, VA 24061, "Influences of Stress State on Hydrogen Embrittlement," ibid.
- 27. M. R. Mitchell, N. E. Paton, R. O. Ritchie, and N. Q. Nguyen, Rockwell International Science Center, Thousand Oaks, CA 91360, "Near-Threshold Fatigue Crack Propagation in Pipeline Steels in High Pressure Environments," ibid.
- 28. G. Strickland, Brookhaven National Laboratory, Upton, NY 11973, "Hydrogen Storage for Automobiles," ibid.
- 29. R. J. Teitel, Robert J. Teitel Associates, San Diego, CA 92123, "Development Status of Microcavity Hydrogen Storage Systems for Automotive Applications," ibid.

Figure 1. Thermochemical cycles whose chemistry and closed loop operation have been verified in the laboratory.

SULFUR-IODINE CYCLE

$$2 \text{ H}_2\text{0} + \text{SO}_2 \times \text{I}_2 \xrightarrow{\text{AQUEOUS}} \text{H}_2\text{SO}_4 + 2 \text{HI}_{\text{X}}$$
 $2 \text{ HI}_{\text{X}} \xrightarrow{573\text{K}} \times \text{I}_2 + \text{H}_2$
 $\text{H}_2\text{SO}_4 \xrightarrow{1144\text{K}} \text{H}_2\text{0} + \text{SO}_2 + 1/2 \text{O}_2$

SULFUR CYCLE (PART ELECTROCHEMICAL)

$$2 H_2^{0} + S0_2 \xrightarrow{\text{AQUEOUS}} H_2 + H_2^{0} + H_2^{0}$$

SULFUR-BROMINE CYCLE (PART ELECTROCHEMICAL)

$$2 \text{ H}_2\text{O} + \text{SO}_2 + \text{Br}_2 \xrightarrow{\text{AQUEOUS}} \text{H}_2\text{SO}_4 + 2 \text{ HBR}$$
 $2 \text{ HBR} \xrightarrow{\text{AQUEOUS}} \text{ELECTROLYSIS} \Rightarrow \text{Br}_2 + \text{H}_2$
 $\text{H}_2\text{SO}_4 \xrightarrow{1000-1100\text{K}} \text{H}_2\text{O} + \text{SO}_2 + 1/2 \text{O}_2$